University of Washington
Department of Chemistry
Chemistry 453
Winter Quarter 2014

Lecture 18 2/3/14

A. Summary of Partition Functions

- The translational partition function is:

$$q_{trans} = \left(\int_0^\infty e^{-n^2h^2/8ma^2} dn \right)^3 = \frac{V}{h^3}\left(2\pi m k_B T\right)^{3/2} \tag{18.1}$$

where particle-in-the-box energies $E_n = \frac{n^2h^2}{8ma^2} << k_B T$ are used to model translations and V=a^3. The vibrational partition function is:

$$q_{vib} = \sum_{n=0}^{\infty} e^{-h\nu(n+1/2)/k_BT} = \frac{e^{-h\nu/2k_BT}}{1-e^{-h\nu/k_BT}} \tag{18.2}$$

where quantized harmonic oscillator energies $E_n = h\nu\left(n+\frac{1}{2}\right)$ are used to model vibrations. The rotational partition function is:

$$q_{rot} = \frac{1}{\sigma}\int_0^\infty (2J+1) e^{-\hbar^2 J(J+1)/2Ik_BT} dJ = \frac{8\pi^2 I k_B T}{\sigma h^2} \tag{18.3}$$

where the quantized rotational energy is $E_J = \frac{\hbar^2}{2I} J\left(J+1\right)$

- Finally, although there are exceptions, the electronic partition function for atoms is generally equal to the degeneracy of the electronic ground state, if we reference to the energy of the ground state and set E$_1$=0:

$$q_{elec} = \sum_{n=1}^{\infty} g_n e^{-E_n/k_BT} \approx g_1 e^{-E_1/k_BT} = g_1 \tag{18.4}$$

B. Molecular Partition Functions for Diatomics

- The molecular partition function is a product of the partition functions for motions 18.1-18.4.

$$\begin{aligned} q &= q_{trans} q_{vib} q_{rot} q_{elec} \\ &= \frac{V}{h^3}\left(2\pi m k_B T\right)^{3/2} \times \frac{e^{-h\nu/2k_BT}}{1-e^{-h\nu/k_BT}} \times \frac{8\pi^2 I k_B T}{\sigma h^2} \times g_1 e^{-E_1/k_BT} \end{aligned} \tag{18.5}$$

- Equation 18.5 is used to define all thermodynamic properties of a molecular substance and is also used to calculate equilibrium constants.
- A great deal of information is required to calculate the molecular partition function: including: the vibration frequency ν, the moment of inertia I, the electronic ground state g$_1$, and the molecular electronic ground state energy E$_1$.

- The vibrational frequency is defined in terms of the vibrational temperature defined as $\theta_{vib} = \frac{h\nu}{k_B}$. For a typical vibrational frequency of $\nu = 10^{14} s^{-1}$ the vibration frequency is

$$\theta_{vib} = \frac{h\nu}{k_B} = \frac{\left(6.62\times10^{-34} Js\right)\left(10^{14} s^{-1}\right)}{1.38\times10^{-23} JK^{=1}} = 4.80\times10^{3} K \qquad (18.6)$$

- Vibrational frequencies are typically at least 10 times room temperature. The physical significance of the value of a vibrational temperature it is the temperature that must be reached before the vibrations of the system behave classically. As shown in Figure 18.1, when the vibrational temperature is exceeded, the vibrational heat capacity approaches its classical value which for a diatomic molecule is Nk$_B$.

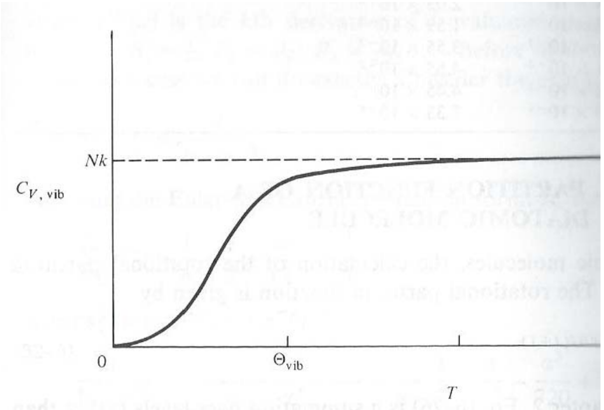

Figure 18.1: When T exceeds θ_{vib} the heat capacity for a one dimensional vibratio approaches Nk$_B$=R, which is the classical limit...

- Using the vibrational temperature formalism the vibrational partition function is

$$q_{vib} = \frac{e^{-\theta_{vib}/2T}}{1 - e^{-\theta_{vib}/T}} \qquad (18.7)$$

- The rotational temperature is similarly defined as $\theta_{rot} = \frac{\hbar^2}{2Ik_B}$. A typical value for the moment of inertia I is 10^{-46} kg m^2. Using this value a typical rotational temperature is

$$\theta_{rot} = \frac{\hbar^2}{2Ik_B} = \frac{\left(1.05\times10^{-34} Js\right)^2}{2\left(10^{-46} kgm^2\right)\left(1.38\times10^{-23} JK^{-1}\right)} \approx 4.06K \qquad (18.8)$$

- This means that for a diatomic molecule the rotational properties approaches classical values when temperature exceeds its rotational temperature. Rotational temperatures are typically lower than room temperature.
- Using equation 18.8 the rotational partition function is

$$q_{rot} = \frac{8\pi^2 Ik_B T}{\sigma h^2} = \frac{2Ik_B T}{\sigma\hbar^2} = \frac{T}{\sigma\theta_{rot}} \qquad (18.9)$$

- The electronic ground state energy E$_1$ is defined as follows. The vibrational potential energy for a real molecular bond is not the simple harmonic expression $V(x) = \frac{1}{2}\kappa x^2$. This is because as the bond stretches to greater lengths, eventually the molecule will dissociated into individual atoms. An empirically derived potential that is more realistic than the simple harmonic potential is the Morse potential, shown in Figure 16.2. The Morse potential has the equation

$$V(x) = D_e\left(1 - e^{\alpha(x-x_e)}\right)^2 \ldots \alpha = \sqrt{\frac{\kappa}{2D_e}} \quad (18.10)$$

Where De is the dissociation energy measured from the classical bottom of the well. Unlike the harmonic potential, the quantized energies for the Morse potential are not equally spaced:

$$E_n = h\nu\left(n+\tfrac{1}{2}\right) - \frac{(h\nu)^2}{4D_e}\left(n+\tfrac{1}{2}\right)^2 \qquad (18.11)$$

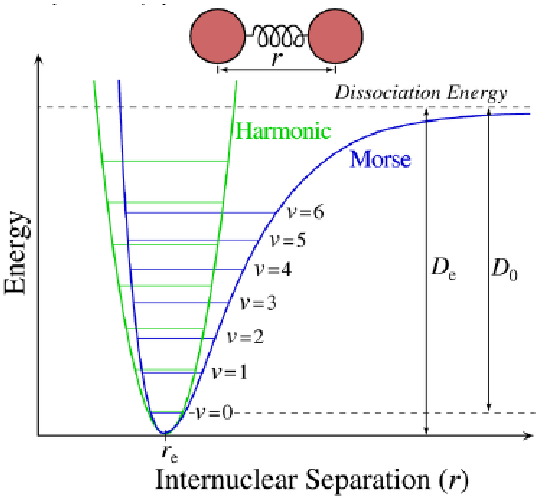

Figure 18.2: Comparison of the harmonic potential and the Morse Potential

- By convention the energies of the individual atoms are zero, as shown in Figure 18.3.
- The ground state electronic energy E_1 is by conventional assigned as the bottom of the classical vibrational well. This energy is defined as the classical dissociation energy and is $-D_e$ relative to the dissociated atomic states, as shown in Figure 18.3.

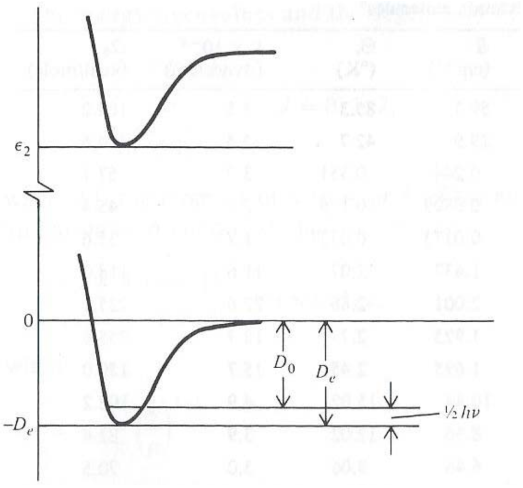

Figure 18.3: The ground electronic state is defined as the bottom of the classical vibrational well or $-D_e$ relative to the dissociated atomic states

- The difference between the dissociated atomic state and the ground vibrational state is defined as D_0

  where $D_e = D_0 + \frac{h\nu}{2}$. Using these definitions the electronic partition function is about equal to:

$$q_{elec} \approx g_1 e^{-E_1/k_BT} = g_1 e^{+D_e/k_BT} \qquad (18.12)$$

- In practice De is usually reported in units of Joules per mole. So id De is given in these units the argument of the exponent in 18.12 is De/RT. Using equation 18.7, 18.9, and 18.12 (with the De/RT in the exponent) the molecular partition function for a diatomic molecule is defined as:

$$\begin{aligned} q &= q_{trans} q_{vib} q_{rot} q_{elec} \\ &= \frac{V}{h^3}\left(2\pi m k_B T\right)^{3/2} \times \frac{e^{-\theta_{vib}/2T}}{1-e^{-\theta_{vib}/T}} \times \frac{T}{\sigma\theta_{rot}} \times g_1 e^{D_e/RT} \end{aligned} \tag{18.13}$$

- Useful parameters for calculating molecular partition functions for common diatomic molecules are given in Table 18.1. Again: note the RT in the argument of electronic exponential term. This is because in table 18.1 D_e is in terms of kJ per mole.

Molecule	$\theta_{vib}\left(K\right)$	$\theta_{rot}\left(K\right)$	ν(x10^{13} s^{-1})	g_1	D_e(kJ mol^{-1})	D_0(kJ mol^{-1})
H_2	6215	85.3	12.960	1	457.6	432.1
Cl_2	808	0.351	1.683	1	242.3	239.2
I_2	308	0.0537	0.642	1	150.3	148.8
CO	3103	2.77	6.471	1	1085	1070
NO	2719	2.45	5.670	2	638.1	626.8
HCl	4227	15.02	8.814	1	445.2	427.8

C. Thermodynamic Properties

- From 18.13 all thermodynamic properties for a diatomic molecule can be determined. For example, the molar internal energy is:

$$\begin{aligned} U &= N_A k_B T^2 \frac{\partial \ln q}{\partial T} = N_A k_B T^2 \frac{\partial}{\partial T}\left[\ln q_{trans} + \ln q_{rot} + \ln q_{vib} + \ln q_{elec}\right] \\ &= \frac{3RT}{2} + RT + \frac{N_A h\nu}{2} + \frac{N_A h\nu}{e^{h\nu/k_B T}-1} - D_e \\ &= \frac{5RT}{2} + \frac{R\theta_{vib}}{2} + \frac{R\theta_{vib}}{e^{\theta_{vib}/T}-1} - D_e \end{aligned} \tag{18.14}$$

- In the last line of equation 18.14 the first term is the internal energy from translations and rotations, both assumed to be in the classical (i.e. high temperature) limit.
- The second term is the contribution from the ground state vibrational energy...the so-called zero point energy.
- The third term comes from the excited vibrational states.
- Finally, the fourth term is the stabilization of the diatomic molecule arising from the sharing of electrons in a covalent chemical bond between the two nuclei. For this reason the fourth is negative and lowers the energy of the molecule relative to the sum of the energies of the separated atoms. D_e is assumed in units of Joules per mole. It is often tabulated, as above in units of kJoules per mole. So be careful!
- The heat capacity can now be obtained by differentiation of equation 18.14:

$$C_V = \frac{\partial U}{\partial T} = \frac{5R}{2} + R\left(\frac{\theta_{vib}}{T}\right)^2 \frac{e^{-\theta_{vib}/T}}{\left(1-e^{-\theta_{vib}/T}\right)^2} \tag{18.15}$$

- Note how the electronic energy makes no contribution to the heat capacity. This is due to the extremely high “electronic temperature” (i.e. >10^5 K) which results in only the ground electronic state being populated at realistic temperatures.